

THE NITRATE TO AMMONIA AND CERAMIC (NAC) PROCESS

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JUN 23 1993
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For presentation at the
1993 Incineration Conference, Knoxville, TN
May 3-7, 1993

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A.J. Mattus and D.D. Lee

ABSTRACT

A new low-temperature (50-60°C) process for the reduction of nitrate or nitrite to ammonia gas in a stirred, ethylene glycol-cooled reactor has been developed at the Oak Ridge National Laboratory. The process has nearly completed 2 years of bench-top testing in preparation for a pilot-scale demonstration in the fall of 1994. The nitrate to ammonia and ceramic (NAC) process utilizes the active metal aluminum (in powder or shot form) in alkaline solution to convert nitrate to ammonia gas with the liberation of heat. In the process, between 0.8 and 1.6 kg of aluminum per kilogram of sodium nitrate is required to convert solutions of between 3.1 and 6.2 M nitrate to near zero concentration, depending upon the processing mode.

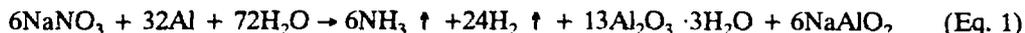
Prior to feeding aluminum metal to the reactor, 40 μm quartz is added based upon the total sodium content of the waste. Upon adding the aluminum metal, a by-product of gibbsite precipitates in the reactor as the ammonia leaves the solution. At the end of the reaction, the alumina-silica-based solids are dewatered, calcined, pressed, and sintered into a hard ceramic. Comparing the volume of the final ceramic product with the volume of the starting waste solution, we obtain an $\sim 70\%$ volume reduction. This compares with an expected 50% volume increase if the waste were immobilized in cement-based grout.

The process is being developed for use at the U.S. Department of Energy's (DOE) Hanford, Washington, site, where as much as 125,000 tonnes of nitrate salts is stored in 4 million liter tanks. Additionally, DOE may be able to shred radioactively contaminated scrap aluminum, available from many of its sites nationwide, and use this metal to feed the NAC reactor at Hanford in the future.

INTRODUCTION

It is well known that aluminum is not stable thermodynamically in the presence of water and oxygen and especially in an alkaline environment. The metal's instability is due to the fact that it dissolves in water to liberate hydrogen; this process is especially vigorous in alkaline solution. Because aluminum coats itself with a very dense protective layer of oxide (gibbsite), it can be maintained for a useful length of time on this planet.

We may take advantage of the reactivity of aluminum to reduce alkaline, nitrate or nitrite-based waste solutions to ammonia gas and highly insoluble gibbsite ($\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$). This reaction of metal with nitrate is shown in Eq. (1):



Although Eq. (1) shows the formation of unwanted hydrogen gas, it should be understood that hydrogen production potential exists at the end of the reaction only, when the nitrate concentration falls to below ~ 3000 ppm. Depending upon the mode of operation, the last 10% of the nitrate in the waste solution might require the same amount of aluminum reactant used for the first 90% due to competition between nitrate and water for aluminum.

The gibbsite product is hard (2.5-3.5 Mohr) and dense (2.42 g/cm³), and upon aging without silica, it hardens and is insoluble in acid and only sparingly soluble in hot caustic. This material is the modern-day component of ceramics, and when fused with silica, it forms a ceramic product with all the inherent properties of such a material (1). In the ceramics industry silica is added to give various desired properties; however, in this process, we add silica to form the mineral-phase nepheline (NaAlSi₃O₈), which binds the sodium component of our sodium nitrate-based waste solution. Prior to the addition of aluminum metal, when operating in the batch mode, silica is added in the form of 40 μm quartz such that we have an equal molar ratio of silicon to sodium, as required by the chemical formula for nepheline.

The dense product from the reactor is easily dewatered, as it is much like sand; it can then be calcined at between 600 and 800°C, uniaxially pressed at 69 MPa (10,000 psi), and sintered in the range of 1300 to 1400°C as is done with other ceramics. Currently, we are obtaining final ceramic forms with densities of ~2.8 g/cm³. Because we are forming a ceramic, we also have the benefit of binding most metals which may be present in the Hanford waste in the solid ceramic phase as spinels, as they are called in the material science field (2). We expect that this means that passing the U.S. Environmental Protection Agency's Toxicity Characteristic Leaching Procedure may be easily accomplished; this type of testing of our product is planned for this year.

Additionally, the size of the gibbsite particles forming *in situ* in our reactor is known to be primarily submicron, based upon the literature and upon observing material pass through filter paper in the laboratory. Because of these small dense particles, we have an opportunity to produce a solid with much smaller pores than those in any cement-based material. Therefore, the capillary pore pressure resistance inside such a solid will be very high as is the case with most ceramics. Water from the outside will not be able to penetrate, as it can with cement-based grout or even with high-grade structural concrete. Small pores and therefore capillary resistance also inhibit the ability of ions to diffuse into or out of such a ceramic product without this necessary water.

NAC PROCESS GENERAL FLOW SHEET

The general flow sheet for the NAC process is presented in Fig. 1. This figure shows the whole integrated process including the formation of the ceramic product.

The discharged product from the reactor is very amenable to microwave drying, calcining, and sintering because it is primarily alumina and silica. If dewatered, dried, calcined, and compacted uniaxially in a container prior to sintering, a hard ceramic may be produced using microwaves in the 28-GHz range.

What is also fortuitous about the use of microwave processing is that alumina is well suited to this technique because it is transparent to microwaves. It has a large "skin depth" (penetration depth), up to 3 to 6 m compared with only a few centimeters into a sodium nitrate-based solution. Use of microwaves means uniform heating and the potential to sinter at much lower temperatures than those possible with conventional convective heating systems.

GENERAL FLOW SHEET FOR THE NITRATE TO AMMONIA AND CERAMIC (NAC) PROCESS

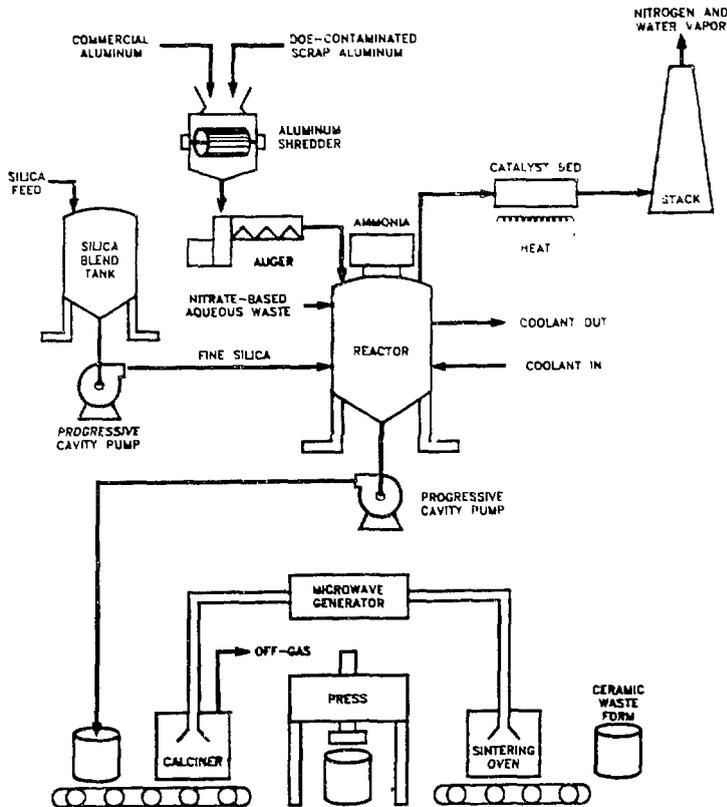


Fig. 1. General flow sheet for the NAC process.

WASTE VOLUME REDUCTION

Upon converting 90 to 99% of all of the nitrate or nitrite present in 3.1 to 6.2 M sodium nitrate solutions to ammonia and upon forming the final ceramic product, we obtain a very large volume reduction. If a nitrate-based waste is immobilized in a cement-based grout, as is done at Savannah River or at Oak Ridge's Melton Valley, we can expect a volume increase of between 35 to 50% depending upon the formulation used. In Oak Ridge's Melton Valley, we are grouting 4 M sodium nitrate and obtaining a 40% increase in volume. Figure 2 shows this relative volume change between cement-based grout and the NAC process.

RELATIVE VOLUME REDUCTION EFFICIENCIES: A COMPARISON OF GROUTING WITH THE NAC PROCESS

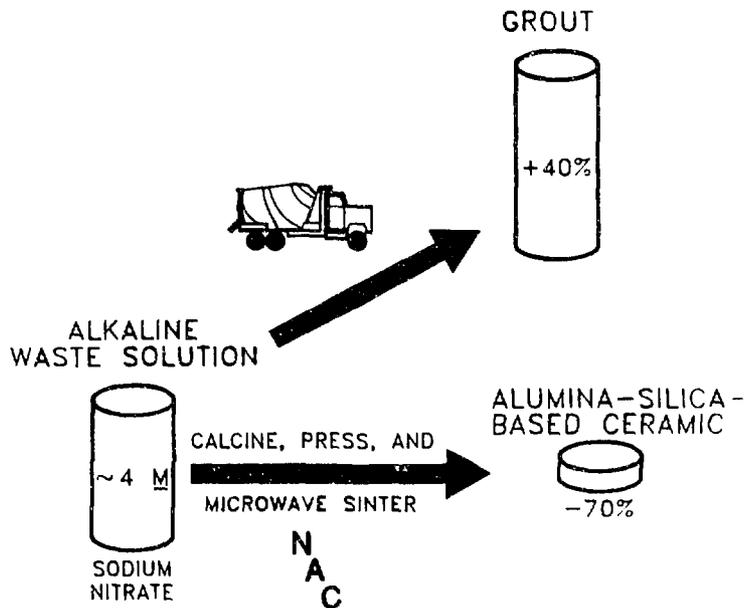


Fig. 2. Relative volume reduction efficiencies of the NAC process compared with cement-based grout.

CONCLUSIONS

The experimental results obtained to date confirm that the NAC process will reduce the nitrate present in Hanford aqueous, sodium nitrate-based waste to ammonia and hydrated alumina. When used in combination with silica, reactor product can be used to produce an alumina-silica-based ceramic. The reaction is exothermic and requires cooling to control the reactor temperature to between 50 and 60°C. Upon using a motorized auger to feed aluminum powder to an ethylene glycol-cooled reactor, we have shown that the reaction can be easily controlled at temperatures between 50 and 60°C.

Utilizing Hanford supernate at concentrations of between 3.1 and 6.2 M sodium nitrate, 90–99% of the nitrate present can be converted to ammonia, the converted percentage being primarily dependent upon the ability of the mixing system in the reactor to stir the solid/liquid slurry when the batch mode is used. If the process is run in the continuous mode, high concentrations of nitrate can be treated at still higher overall efficiencies.

Bench-top experiments showed that aluminum can be pumped to the reactor as a slurry of aluminum powder and water, in addition to using a motorized auger. The water-slurry feed has the advantage of adding needed water to the reactor to replace the water taken up as the aluminum reacts to form crystalline gibbsite.

Addition of the aluminum to the reactor in the form of larger particles reduced problems encountered with the fine dry powder feed by preventing caking from water vapor condensation. The larger particles of aluminum also reacted more slowly than the fine powders and required less cooling and temperature control.

Reaction rates for the various experiments were calculated to give a rough idea of what might be expected for a pilot-plant design. The rates were based upon a differential nitrate reduction at a point in the reaction where nitrate was being actively reduced, usually at a point when between 70 and 150% of the theoretical amount of aluminum had been added. These rates were between 80 and 300 grams of NaNO_3 per liter of starting reactor volume per hour. Based upon these numbers, a preliminary estimate was made for a full-size plant to treat the Hanford single-shell tank waste at 1200 kilograms of NO_3 per hour over a 20-year period. The engineering cost estimate and its assumptions are presented in the appendix of our draft report on work performed last year; the report is available upon request (3).

The cost estimate for a full-scale nitrate processing plant assumes a batch reactor with unit costs of between \$2.01 and \$2.66/kg of nitrate to process the Hanford nitrate waste over 20 years. The cost of aluminum is a major part of the overall cost, making reaction efficiency even more important. The operating cost compares with published literature costs for the electrolytic process and thermal processing in 1957 of \$5.13/kg of nitrate.

Results of this study have shown that the product exiting the reactor can be uniaxially pressed as any other ceramic to result in a 70% volume reduction based upon the starting volume of the original waste solution. All the water associated with the waste solution is consumed by the aluminum to form oxide.

The effective treatment of the Hanford nitrate-based wastes is dependent upon the development of simple and effective technologies such as described in this work. Continued work in FY 1993 will focus upon the waste form properties such as leaching resistance for sodium and many other species of interest to Hanford.

REFERENCES

1. P.P. BUDNIKOV, P. P., *The Technology of Ceramics and Refractories*, trans. Scripta Technica, The MIT Press, Cambridge, MA (1964).
2. L.H. VAN VLACK, *Elements of Material Science and Engineering*, 5th ed., Addison-Wesley Pub. Co., Reading, MA (1985), p. 261.
3. A.J. MATTUS, D.D. LEE, et al., "A Low-Temperature Process for the Denitration of Hanford Single-Shell Tank, Nitrate-Based Waste Utilizing the Nitrate to Ammonia and Ceramic (NAC) Process," ORNL/TM-12245, Oak Ridge National Laboratory, Oak Ridge, TN (1993).